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PLASMA HEATING OF A SUBSTRATE WITH SUBSEQUENT HIGH TEMPERATURE ETCHING

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PLASMA HEATING OF A SUBSTRATE WITH SUBSEQUENT HIGH TEMPERATURE ETCHING

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BACKGROUND OF THE INVENTION

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1. Field of the Invention

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The present invention pertains to a method of plasma heating a substrate and then etching the substrate, where deposits generated during plasma heating are removed so that control over a critical dimension of an etched feature is maintained.

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2. Brief Description of the Background Art

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Maintaining a substrate at a particular temperature during semiconductor processing frequently enables control of the critical dimension of a feature on the substrate. Processing may involve chemical vapor deposition (CVD), physical vapor deposition (PVD), or plasma etching, for example.

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In a plasma etching process, a substrate is typically placed on an electrostatic chuck in an etch reactor in which the substrate is exposed to an etchant plasma. The temperature of the substrate may be controlled using a gas in contact with the backside of the substrate. When the gas in contact with the substrate is at a lower temperature than the substrate, so that it acts as a coolant, the substrate may be allowed to heat by a reduction of the pressure of the coolant gas. Specifically, when the pressure of the gas in contact with the backside of the substrate is reduced, the rate of heat removal is decreased, and thus the temperature of the substrate is increased.

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Other methods for heating a substrate to a desired temperature include use of a resistive heating element embedded in the electrostatic chuck. The heated chuck may be used in combination with a coolant gas to adjust the substrate temperature.

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One method for heating a substrate surface involves the use of ion bombardment of

1   the substrate surface during semiconductor processing. RF coupled or microwave energy

2   may be used to produce a plasma which is the source of ions which come in contact with the

3   substrate. A biasing power may be applied to the substrate to attract ions toward the

4   substrate, to provide a more rapid heating of the substrate. However, use of a substrate bias

5   to attract ions toward the substrate generally causes sputtering of more malleable materials

6   on the substrate surface, such as metals. Thus, when a metal layer is being etched, for

7   example, a portion of the metal layer is typically sputtered up onto the sidewalls of an

8   overlying patterned mask which is used to provide patterned etching of the metal layer.

9   Subsequent removal of the sputtered material has proven difficult. In an attempt to reduce

10   or avoid sputtering of surface materials during plasma heating of a substrate surface, various

11   gases have been used as the plasma source gas, to lessen the sputtering effect. Specifically,

12   it has been recommended that the gas used to form the plasma be composed of one or more

13   gases including, for example, oxygen, argon, silane, silicon tetrafluoride, helium, neon,

14   krypton, xenon, nitrogen, or mixtures thereof. Nitrogen gas is said to produce less

15   satisfactory results, with the material being heated possibly forming nitrides, similar to the

16   manner in which oxides are produced when an oxygen plasma is used.

17   In some instances, it has been recommended that no substrate biasing be used, and

18   that a lower heating rate be accepted. The use of a substrate heating plasma generated using

19   only microwave energy is said to reduce the amount of sputtering of a substrate surface.

20   For instance, when an RF bias is applied to a substrate having a SiO_2 surface, the sputter rate

21   of the SiO_2 is said to be on the order of 1000 Å per minute, but when no substrate bias is

22   applied, and the only energy applied is microwave energy used to produce the plasma, the

23   sputter rate is said to be reduced well over 50%.

24   Substrate temperature control is an important factor in the control of critical

25   dimensions of a feature during plasma etching of the feature. For instance, during etch

26   processing, the materials from a portion of the layer that is etched, as well as compounds

1   formed by a combination of the etchant gases and the layer materials, may coat the sides of

2   the patterned mask overlying the feature which is being etched, or may coat the sides of the

3   feature being etched and thereby reduce the size of the opening through which etching

4   occurs. This may result in an increase in the size of the feature produced during etching and

5   may result in an etch profile which is different from the top to the bottom of the etched

6   feature. Such growth of a feature dimension and variation in feature sidewall profile may

7   be critical and may detrimentally affect the functionality of the features. By increasing the

8   temperature of the substrate during processing, etch byproducts remain more volatile, and

9   control over etch sidewall profile, as well as growth of critical feature dimensions, may be

10   achieved.

11   High substrate temperature etching is advantageous when the materials being etched

12   are either metal or metal-containing compounds which are of low volatility, such as, for

13   example, platinum, copper, iridium, iridium dioxide, lead zirconium titanate, ruthenium,

14   ruthenium dioxide, barium strontium titanate, and bismuth strontium tantalate.

15   In summary, although it is possible to reduce sputtering during plasma heating of

16   substrates by reducing substrate biasing, this substantially slows the heating process. The

17   use of resistance heaters in the electrostatic chuck under the substrate is expensive and

18   decreases the response time when it is desired to stop heating or to cool the substrate.

19   Accordingly, there remains a need for a substrate heating method that provides rapid

20   substrate heating while reducing the effect of material sputtered during the heating process

21   on the critical dimension and sidewall profile of an etched feature.

22   ## SUMMARY OF THE INVENTION

23   We have discovered a method of reducing the effect of material sputtered/etched

24   during the heating of a substrate.

25   One embodiment of the method pertains to preheating a substrate which includes a

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1 metal-containing layer which is to be pattern etched subsequent to preheating. The method
2 includes exposing the substrate to a preheating plasma which produces a deposit or residue
3 during preheating which is more easily etched than said metal-containing layer during the
4 subsequent plasma etching of said metal-containing layer.

5   In another embodiment, plasma heating of a substrate and subsequent etching of a
6 metal-containing layer included in said substrate is carried out while maintaining control
7 over a critical dimension of a feature etched in the metal-containing layer. In particular, the
8 method includes:

9   a)   supplying a first plasma source gas to a process chamber containing a
10 substrate, wherein the first plasma source gas is used to generate a plasma which is used to
11 preheat the said substrate, and wherein the plasma source gas contains at least one gas which
12 is slightly reactive with the metal-containing layer;

13   b)   preheating the substrate to a temperature of at least 150 °C using ion
14 bombardment from the first plasma;

15   c)   supplying a second plasma source gas which generates a plasma used to etch
16 the metal-containing layer; and

17   d)   etching the metal-containing layer, wherein essentially all of a residue
18 generated during the preheating of the substrate is removed during the etching of the metal-
19 containing layer.

20   BRIEF DESCRIPTION OF THE DRAWINGS
21   Figure 1A shows an etched stack of layers (100) including a patterned hard mask
22 layer (108) overlying a platinum-containing layer (106), which overlies a titanium nitride
23 layer (104), which overlies a silicon oxide layer (102). Residue material (110) produced
24 by sputtering during preheating of the substrate and during patterned etching of the stack of
25 the layers (100) resides on the sidewalls (112).

1   Figure 1B shows the etched stack of layers of Figure 1A after treatment with a
2 diluted HF solution to remove patterned hard mask layer (108). The etched structure
3 produced (120) includes platinum-containing layer (106) overlying titanium nitride layer
4 (104), which overlies silicon oxide layer (102). Sputtered material (110) has collapsed upon
5 itself after removal of residual silicon oxide hard mask layer (108).

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7   Figure 2A shows an etched stack of layers (200) including a patterned silicon oxide
8 hard mask layer (208) overlying a platinum-containing layer (206), which overlies a titanium
9 nitride layer (204), which overlies a silicon oxide layer (202). No sputtered material
10 remains on etched sidewalls (212) after patterned etching of the stack of the layers (200).

11   Figure 2B shows the etched stack of layers of Figure 2A after treatment with a
12 diluted HF solution to remove patterned hard mask layer (208). The etched structure
13 produced (220) includes platinum-containing layer (206) overlying titanium nitride layer
14 (204), which overlies silicon oxide layer (202). There was no residual sputtered material
15 on the sidewalls (212) of etched silicon oxide hard masking layer (208). There was no
16 apparent residual sputtered material on the sidewalls (214) of the etched platinum layer
17 (206).

18   Figure 3 shows the time-temperature correlation during a substrate preheating step,
19 where the preheating plasma is formed from nitrogen gas and the substrate is a stack of
20 layers of the kind described with reference to Figure 1A, but prior to patterned etching.

21   Figure 4A shows an etched stack of layers (400) including a patterned silicon oxide
22 hard mask layer (408) overlying a platinum-containing layer (406), which overlies a titanium
23 nitride layer (404), which overlies a silicon oxide layer (402). Residue material (410)

1   produced by sputtering during preheating of the substrate and during patterned etching of

2   the stack of the layers (400) resides on the hard mask sidewalls (412), as well as on the

3   sidewalls (414) of platinum-containing layer (406).

4   Figure 4B shows the etched stack of layers of Figure 4A after treatment with a

5   diluted HF solution to remove patterned silicon oxide hard mask layer (408). The etched

6   structure produced (420) includes platinum-containing layer (406) overlying titanium nitride

7   layer (404), which overlies silicon oxide layer (402). Residue material (410) has collapsed

8   toward the exterior of sidewalls (414).

9   Figure 5A shows an etched stack of layers (500) including a patterned silicon oxide

10 hard mask layer (508) overlying a platinum-containing layer (506), which overlies a titanium

11 nitride layer (504), which overlies a silicon oxide layer (502). Residue material (510)

12 produced by sputtering during preheating of the substrate and during patterned etching of

13 the stack of the layers (500) resides on the hard mask sidewalls (512), as well as on the

14 sidewalls (514) of platinum-containing layer (506). There is so much residual material (510)

15 that it even covers the upper surface (516) of hard mask layer (508).

16 Figure 5B shows an etched stack of layers (520) produced without a substrate

17 preheating step. The layer stack was the same as that of Figure 5A, and the etchant used

18 during plasma etching of the platinum-containing layer was the same as the etchant used to

19 etch the layer stack shown in Figure 5A. No residual material was observed on the exterior

20 surfaces of patterned silicon oxide hard mask layer (508) sidewall (512), nor on the exterior

21 surfaces of etched platinum-containing layer (506) sidewall (514).

22 Figure 6 shows an example of an apparatus which can be used to carry out the

1 etching processes described herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

2 Described in detail below is a method of reducing the effect on etched feature critical
3 dimensions of material sputtered during the heating of a substrate. As a preface to the
4 detailed description, it should be noted that, as used in this specification and the appended
5 claims, the singular forms "a", "an", and "the" include plural referents, unless the context
6 clearly dictates otherwise.

8 We have discovered a method of reducing the effect of material sputtered/etched
9 during the heating of a substrate. This permits the use of ion bombardment to heat substrates
10 despite the fact that the ion bombardment may sputter/etch features on the substrate causing
11 deposits and residue to form on features within the substrate.

12 It is crucial in the production of submicron-sized devices that critical dimensions be
13 maintained during the etching of a semiconductor feature. When the feature to be etched
14 requires high temperature etch conditions, it is necessary to preheat the substrate before
15 beginning the feature etching, so that etch by-products are sufficiently volatile. Ion
16 bombardment heating of a substrate which leads to sputtering/etching of an exposed layer
17 which is to be etched is possible without affecting the critical dimension of the etched
18 feature if the plasma source gas used for heating enables the subsequent removal of
19 substantially all of the sputtered/etched material generated during the preheating step. The
20 sputtered/etched residue from preheating is removed during the etch step which follows the
21 preheating of a substrate, for example.

22 To enable removal of a preheating sputtered/etched material residue, the plasma
23 source gas used to generate the preheating plasma may provide a plasma which is slightly
24 reactive with at least the exposed layer which is to be subsequently etched. Frequently the
25 exposed layer is a metal. For example, and not by way of limitation, in the etching of

1   platinum-comprising material, iridium-comprising material, and ruthenium-comprising

2   material, the preheating plasma is slightly reactive with the metal-comprising material.

3   It may also be advantageous to have the preheating plasma source gas contain a gas

4   which is slightly reactive with the patterned masking material which overlies the layer

5   exposed for etching. This is the case when the masking material is capable of providing

6   reactive species which react with the material sputtered/etched from the exposed layer

7   during the preheating step.

8   No single plasma source gas combination will produce the desired etch results on all

9   substrates. Thus, for a given material layer to be pattern etched, one skilled in the art should

10 select a combination of plasma source gases for the etch step which will provide an

11 acceptable etch rate and etch selectivity with respect to substrate materials adjacent to the

12 material which is being pattern etched, and meet other required etch criteria. Once the

13 combination of gases to be used during the patterning etch step has been determined, the

14 particular plasma source gas to be used during preheating of the substrate is selected. The

15 plasma source gas for substrate preheating may be a single gas or a combination of gases,

16 but needs to include at least one gas which is at least slightly reactive with the substrate

17 material to be etched. Preferably, the plasma source gas for generation of the substrate

18 preheating plasma contains at least one gas from the combination of etchant plasma gases

19 used in the subsequent etching of the substrate material, as this simplifies processing

20 requirements.

21   This inventive method provides a relatively quick way of heating a substrate without

22 using a resistance heater in an electrostatic chuck, thereby avoiding the added cost of such

23 equipment and the undesired effects when needing to cool the substrate. Further, this

24 inventive method is not focused on eliminating the sputtering of material during a substrate

25 preheating step, but rather is focused on removing the material that is sputtered during the

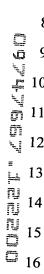26 preheating step during the patterned etching step.

1   I.   AN APPARATUS FOR PRACTICING THE INVENTION

2   The embodiment etch processes described herein were carried out in a CENTURA®

3 Integrated Processing System, available from Applied Materials, Inc., of Santa Clara,

4 California. The system is shown and described in U.S. Patent No. 5,186,718, the disclosure

5 of which is hereby incorporated by reference. Although the etch process chamber used in

6 the Examples presented herein is shown in schematic in Figure 6, any of the etch processors

7 available in the industry should be able to take advantage of the etch chemistry described

8 herein, with some adjustment to other process parameters. The equipment shown in

9 schematic in Figure 6 includes a Decoupled Plasma Source (DPS) of the kind described by

10 Yan Ye et al. at the Proceedings of the Eleventh International Symposium of Plasma

11 Processing (May 7, 1996) and published in the *Electrochemical Society Proceedings*

12 (Volume 96-12, pp. 222 - 233, 1996), which is hereby incorporated by reference. The

13 plasma processing chamber enables the processing of an 8 inch (200 mm) diameter wafer.

14   Figure 6 shows a schematic of a side view of an individual CENTURA® DPS™

15 metal etch chamber 600. The etch chamber 600 consists of an upper chamber 604 having

16 a ceramic dome 606, and a lower chamber 608. The lower chamber 608 includes a

17 monopolar electrostatic chuck (ESC) cathode 610. Gas is introduced into the chamber via

18 gas injection nozzles 614 for uniform gas distribution. Chamber pressure is controlled by

19 a closed-loop pressure control system (not shown) using a throttle valve 618. During

20 processing, a substrate 620 is introduced into the lower chamber 608 through inlet 622. The

21 substrate 620 is held in place by means of a static charge generated on the surface of

22 electrostatic chuck (ESC) cathode 610 by applying a DC voltage to a conductive layer (not

23 shown) located under a dielectric film (not shown) on the chuck surface. The cathode 610

24 and substrate 620 are then raised by means of a wafer lift 624 and sealed against the upper

25 chamber 604 in position for processing. Etch gases are introduced into the upper chamber

1   604 via gas injection nozzles 614. The etch chamber 600 uses an inductively coupled

2   plasma source power 626 and matching network 628 operating at about 2.0 MHZ for

3   generating and sustaining a high density plasma. The wafer is biased with an RF source 630

4   and matching network 632 operating at about 13.56 MHZ. Plasma source power 626 and

5   substrate biasing means 630 are controlled by separate controllers (not shown).

6   II.   THE METHOD OF THE INVENTION FOR PLASMA HEATING AND
7   ETCHING A SUBSTRATE WHILE MAINTAINING CRITICAL DIMENSION

8   The present invention pertains to a method of reducing the effect on etched feature

9   critical dimensions and etched sidewall profile, which results from the presence of residue

10   produced during an ion-bombardment heating of the substrate in which the feature resides.

11   The sputtered material from the preheating step is removed during the subsequent etching

12   of the substrate.

13   A patterned hard mask layer may be used in plasma etching to cover portions of the

14   underlying substrate layer, while leaving other portions of the layer exposed to an etchant

15   plasma.   A hard masking layer is typically used for patterned etching of underlying layers

16   when the layer to be etched is one which requires high temperature etching to obtain a

17   reasonable etch rate or selectivity, or where the etch by-products are non-volatile and require

18   a higher temperature substrate to reduce the amount of by-product which remains on the

19   etched surfaces after completion of the etch process. Many of the metal layers deposited to

20   form conductive structures require the use of a patterned hard mask layer rather than a

21   photoresist, due to the substrate temperature required to produce the desired etch results.

22   Examples, not by way of limitation, of metals or metal-containing compounds which require

23   a high temperature substrate during etching include platinum, iridium, iridium dioxide,

24   ruthenium, and ruthenium dioxide. Typically these metals are used in the formation of

25   capacitor electrodes, gate electrodes, contacts, and other conductive structures.

1   During the development of the present method, we performed numerous

2   experiments to determine the typical amount of material sputtered onto the vertical sidewalls

3   of a patterned hard masking layer during a substrate (etch stack) preheating step. Table One,

4   below, shows various examples of plasma source gases used to produce the preheating

5   plasma, and a description of the appearance of the sidewall profile of the patterned hard

6   mask after completion of the preheating step. The etch stack was as previously described

7   with reference to Figure 1, where the patterned hard mask layer is a bi-layer, as described

8   in detail below.

9   Table One. Preheated Platinum-Containing Substrate - Hard Mask Sidewall Profile

Run #	1	2	3	4	5
N_2 Preheat Gas (sccm)	50	--	100	--	15
O_2 Preheat Gas (sccm)	--	--	--	100	--
Ar Preheat Gas (sccm)	50	100	--	--	30
Cl_2 Preheat Gas (sccm)	--	--	--	--	120
Hardmask Sidewall Profile	Essentially Vertical (Light Build-up)	Slightly Tapered (Moderate Build-up)	Essentially Vertical (Light Build-up)	Essentially Vertical (Light Build-up)	Very Tapered (Heavy Build-up)

17   Each substrate was preheated for about 45 seconds. Other preheating parameters

18   included a process chamber pressure of about 20 mTorr; an RF substrate bias power of about

19   500 W; an RF plasma source power of about 1800 W; and a cathode temperature of about

20   80°C.

21   With reference to Figure 1, from bottom to top of the etch stack, the bottom layer of

22   silicon oxide (SiO_x) 102 was about 8000 Å thick, the overlying barrier layer of titanium

23   nitride (TiN) 104 was about 200 Å thick, the platinum (Pt) -comprising layer 106 was about

24   2500 Å thick, and the patterned hard mask layer 108 was a bi-layer (not shown as a bilayer

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in Figure 1), where the bottom layer was about 300 Å of TiN, and the top, overlying layer was about 5000 Å of TEOS produced silicon oxide (SiO_x). The underlying metal layer was platinum.

The term "hardmask sidewall profile", as used in Table One, refers to the cross-sectional profile of the hard mask and to the angle of the patterned mask sidewall after a substrate preheating step, relative to an underlying horizontal substrate. When large amounts of material sputter during plasma preheating of the etch stack (substrate), such sputtered material tends to build-up at the base of the patterned hard mask, forming a wedge-shaped hard mask sidewall. This wedge shape tends to continue downward during etching of an underlying metal layer, affecting the sidewall profile of the etched metal layer and the critical dimensions of the etched metal features. With reference to Table One, the hard mask profiles were studied after a preheat step and prior to etching of an underlying metal layer in order to evaluate the amount of material deposited on the vertical sidewall of the patterned hard mask during the preheating step, when different plasma source gases were used during the preheating step.

The best hard mask sidewall profiles were obtained in Runs # 1, # 3, and # 4. When the plasma source gas during substrate preheating was made up from a mixture of nitrogen and argon gas, with a high (50 %) concentration of nitrogen, or was nitrogen, or oxygen, respectively, the hard mask profile was essentially vertical, indicating only a light build-up of sputtered material. However, when argon gas, or a combination of nitrogen, argon, and chlorine gas, represented by Runs # 2 and # 5, respectively, was used as the plasma source gas for generation of the plasma used to preheat the substrate, the profile was significantly tapered. Thus, a wedge-like vertical layer of sputtered material was deposited on the hard mask sidewall. In Run #2, the plasma source gas used during substrate preheating was essentially non-reactive with both the exposed platinum layer and with the overlying silicon oxide hard masking material. In Run # 5, nearly 73 % of the plasma source gas used during

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1　substrate preheating was Cl_2, which is highly reactive with the exposed platinum layer and

2　which is moderately reactive with the overlying silicon oxide hard masking material.

3　　　Experiments were then performed to determine the final etch profile for etch stacks

4　in which the etch stack (substrate) was preheated using a plasma generated from one plasma

5　source gas, and the platinum-containing layer was pattern etched using a plasma generated

6　from another plasma source gas. The results of these experiments are presented in Table

7　Two, below.

8　Table Two.　Preheated and Plasma-Etched Platinum-Containing Layer - Etch Profile

Run #	1	2	3
N_2 Preheat Gas (sccm)	100	--	--
O_2 Preheat Gas (sccm)	--	50	100
Ar Preheat Gas (sccm)	--	50	--
Cl_2, Pt Etch Gas (sccm)	120	120	120
N_2, Pt Etch Gas (sccm)	15	15	15
Ar, Pt Etch Gas (sccm)	30	30	30
Etch Profile	Essentially Vertical	Tapered	Tapered

17　　　Each substrate was preheated for about 45 seconds. Further preheating parameters

18　include a chamber pressure of about 20 mTorr; a substrate bias power of about 500 W; a

19　plasma source power of about 1800 W; and a cathode temperature of about 80 °C. The etch

20　stack was the same as that described above with reference to Table One.

21　　　Patterned etching of the platinum layer was carried out until the platinum etch

22　completion was detected by an optical endpoint detector, then an overetch was carried out

23　for an additional 30 seconds. The pressure in the etch chamber was about 20 mTorr; the

24　substrate bias power applied was about 275 W; the plasma source power was about 900 W;

25　and the cathode (substrate pedestal) temperature was about 80 °C. As previously mentioned,

1   the platinum-containing layer had a thickness of about 2500 Å.

2   The best etch profile was obtained in Run # 1. Only nitrogen gas was used as the

3   plasma source gas during preheating of the substrate; nitrogen gas was also contained in the

4   source gas used for generating the platinum etchant plasma. Virtually no residue remained

5   on the hard mask at the completion of etching, and a vertical etch profile was obtained.

6   However, when a combination of oxygen and argon gas was used as the plasma source gas

7   during preheating of the substrate (Run # 2), residue did remain on the surfaces of the hard

8   mask and etched platinum feature at the completion of the platinum etching. A tapered

9   profile was observed. When only oxygen gas was used as the plasma source gas during

10   preheating of the substrate (Run # 3), a similar, but slightly thicker residue was observed on

11   the hard mask and etched platinum features. Again, a tapered profile was observed.

12   Applicants used the etch plasma source gas and etch process conditions described

13   in Table Two to etch the platinum layer in the same etch stack, where the substrate was not

14   preheated using plasma heating, but was heated using a "hot" electrostatic chuck (heated by

15   an embedded resistive heater). No residue was observed on the hard mask surfaces, nor on

16   the etched platinum surfaces. This indicates that the residue in Run #2 or Run #3 occurs

17   when sputtered platinum-containing material generated during a plasma preheating step is

18   not removed during the subsequent etching of the platinum layer.

19   Applicants concluded, based on the above experimentation, that once a satisfactory

20   plasma source gas is developed for etching a metal layer such as platinum, the plasma source

21   gas used for plasma preheating of the substrate may advantageously contain a gas which is

22   used in etching the metal layer. However, the preheating plasma overall reactivity with the

23   metal layer material must be controlled. If the reactivity is insufficient, built up residue from

24   the preheating step may be so difficult to remove that it remains during the metal etch step,

25   to cause problems with etch profile. If the reactivity is too great, the amount of built up

26   residue present after the preheating step may be such a large quantity that it cannot be
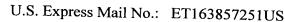
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1   adequately removed during the metal etch step, again causing problems with the etch profile.

2   As used herein, a "lightly reactive" or "slightly reactive" plasma refers to a plasma which

3   provides sufficient reactivity with the exposed layer to be etched (one of the metals

4   described above, for example) that the sputter/etch byproduct produced during preheating

5   of the substrate is more easily etched than the pure exposed layer (metal) during the

6   subsequent etch of the exposed layer.

7   For example, and not by way of limitation, in the etching of platinum, the slightly

8   reactive plasma to be used in a substrate preheating step should be capable of etching a pure

9   platinum layer at an etch rate of at least about 200 Å per minute. For example, if nitrogen

10   alone was used to plasma etch a platinum layer, a maximum platinum etch rate of about 290

11   Å per minute would be expected. One skilled in the art, after reading applicants' disclosure

12   will understand that it is important to use a plasma source gas (which may be a combination

13   of gases) which generates a preheating plasma which is slightly reactive with the exposed

14   layer to be etched. As previously mentioned herein, the preheating plasma may also be

15   slightly reactive with an overlying hardmasking layer, if the hardmasking material will

16   produce reactive species which react with the material sputtered from the exposed layer

17   during the preheating step, thereby generating a sputtered/etched residue which is more

18   easily removed during the subsequent etch step.

19   Although the hard masking material described herein with reference to the etching

20   of platinum is silicon oxide, it is not applicants' intent to be limited to this hard masking

21   material, as other metal containing hard masking materials such as TiN, SiN, TiO_2, or high

22   temperature organic masking materials such as "α-C" polymers (high temperature

23   amorphous carbon-comprising materials) and "α-FC" polymers (high temperature

24   fluorocarbon materials) and FLARE™ (a polyarylene ether, available from Allied Signal,

25   Advanced Microelectronic Materials, Sunnyvale, California) are also contemplated.

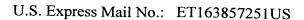26   In the above examples, minimum residue after platinum etching was observed when

1   nitrogen was present in both the plasma source gas used during substrate preheating and the

2   plasma source gas used during platinum etching. One might then believe that chlorine could

3   be used in the plasma source gas for preheating of the substrate; however, the data show that

4   when chlorine is used, at least in a substantial amount, during substrate preheating, large

5   amounts of residue are produced on the hard mask sidewalls. These large amounts of

6   residue distort the hard mask sidewall surfaces (the mask sidewall profile), so that the

7   openings through which the metal can be etched do not enable etching of the metal layer to

8   the desired critical dimensions (even if it were possible to gradually remove the residue

9   during etching of the metal layer). This indicates that when the plasma used for preheating

10   the substrate is highly reactive with the metal layer, this does not provide a good overall

11   result in terms of the etched feature. Thus, the use of chlorine as the major component of

12   a preheating plasma source gas is not advisable.   However, the presence of small amounts

13   of highly reactive gases in a source gas, so that the plasma itself is only slightly reactive with

14   the exposed layer to be etched may be acceptable. As used herein, the term "highly reactive"

15   plasma, with respect to the etching of platinum is a plasma which produces a platinum etch

16   rate in excess of about 800 Å per minute. For example, if a plasma generated from a solely

17   chlorine source gas was used to plasma etch a platinum layer, a platinum etch rate of at least

18   about 800 Å per minute would be expected, using the other process conditions and the

19   process apparatus described above.

20   In view of the data obtained for platinum, the preheating plasma should be capable

21   of etching the material which is to be pattern etched at an etch rate ranging between about

22   200 Å per minute and about 800 Å per minute, preferably at an etch rate ranging between

23   about 250 Å per minute and about 600 Å per minute. One skilled in the art will be able to

24   adjust the plasma source gas compositions and overall process conditions in their particular

25   apparatus to achieve a desired result for a given material to be pattern etched in view of the

26   disclosure provided herein.

16

1   When a non-reactive gas, typically an inert gas such as helium, argon, krypton, or

2   xenon, is used as the sole plasma source gas for substrate preheating, moderate amounts of

3   residue remained after the subsequent metal etch. When a combination of a non-reactive gas

4   and a lightly reactive gas (argon/nitrogen) was used as the plasma source gas for substrate

5   preheating, light to moderate amounts of residue remained after the subsequent metal etch.

6   The best results were obtained when the lightly reactive gas (nitrogen) was used as the sole

7   plasma source gas for substrate preheating. However, the preheating plasma source gas may

8   contain a limited amount of a gas which is essentially non-reactive, as a diluent within the

9   plasma source gas.   A minor amount of experimentation would be required to determine

10   how much diluent gas can be used and still provide a sputtered/etched residue which is more

11   easily removed during the etch step than a pure residue of the exposed material which is to

12   be etched during the etch step.

13   The principles discussed above are best illustrated with reference to the Figures

14   provided herein. Figure 1A shows the etch profile obtained for an etch stack (a substrate)

15   including, from top to bottom, the bi-layer patterned hard mask 108 previously described,

16   overlying a platinum-containing layer 106, which overlies a titanium nitride layer 104,

17   which overlies a silicon oxide layer 102. Residue material 110 produced by sputtering

18   during preheating of the substrate and during patterned etching of the stack of the layers 100

19   remains on the sidewalls 112. The substrate was preheated using a plasma generated solely

20   from O_2. The platinum-containing layer 106 was etched using the $Cl_2/N_2/Ar$ plasma source

21   described in Table Two. The process conditions were as described previously, above.

22   Figure 1B shows the substrate of Figure 1A after being exposed to a diluted HF

23   solution (typically about a 6:1 ratio of H_2O : HF). From Figure 1B, one can see how the

24   sputtered material 110 on the vertical sidewalls 112 of the patterned hard mask 108

25   collapsed on top of the etched platinum layer 106 once the hard mask was removed by the

26   diluted HF solution.

1   Figure 2A shows the etch profile obtained for an etch stack (a substrate) including

2   from top to bottom, the bi-layer patterned hard mask 208 previously described, overlying

3   a platinum-containing layer 206, which overlies a titanium nitride layer 204, which overlies

4   a silicon oxide layer 202. No residue material was observed on the sidewalls 212 of the

5   hard mask 208, nor on the sidewalls 214 of the etched platinum-containing layer 206, after

6   completion of etch of the platinum-containing layer 206. The substrate was preheated using

7   a plasma generated solely from N_2, which produced a slight sputtered build-up, as indicated

8   for Run # 3 in Table One. The platinum-containing layer 206 was etched using the same

9    $Cl_2/N_2/Ar$ etchant plasma described with reference to Figure 1A. At the completion of etch

10   of the platinum-containing layer 206, the slight build-up of sputtered material from the

11   substrate preheating step had been removed.

12   Figure 2B shows the substrate of Figure 2A after exposure to a diluted HF solution.

13   Figure 2B clearly illustrates that virtually all of the sputtered material was removed during

14   the platinum-containing layer plasma etch step.

15   Figure 3 illustrates the heating rate for preheating of the etch stack described above

16   when nitrogen alone is used as the plasma source gas for the preheating plasma. One skilled

17   in the art will appreciate that this is a competitive heating rate for plasma preheating of a

18   substrate.

19   Figure 4A shows the etch profile obtained for an etch stack (a substrate) including

20   from top to bottom, the bi-layer patterned hard mask 408 previously described, overlying

21   a platinum-containing layer 406, which overlies a titanium nitride layer 404, which overlies

22   a silicon oxide layer 402. Residue material 410 produced by sputtering during preheating

23   of the substrate, and during patterned etching of the stack of the layers 400 resides on the

24   sidewalls 412 of hard mask 408 and on the sidewalls 414 of etched platinum-containing

25   layer 406. The substrate was preheated using a plasma generated from 50 sccm of Ar and

26   50 sccm of N_2, and is referenced in Table One as Run # 1. The platinum-containing layer
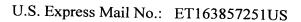
1   406 was etched using the $Cl_2/N_2/Ar$ plasma source described in Table Two. The process

2   conditions were as described previously, above.

3   Figure 4B shows the substrate of Figure 4A after exposure to a diluted HF solution.

4   From Figure 4B, one can see how the sputtered material 410 which was on the vertical

5   sidewalls 412 of the patterned hard mask 408 collapsed about the exterior surfaces of etched

6   platinum-containing layer 406 once the hard mask was removed.

7   Figure 5A shows the etch profile obtained for an etch stack (a substrate) including,

8   from top to bottom, the bi-layer patterned hard mask 508 previously described, overlying

9   a platinum-containing layer 506, which overlies a titanium nitride layer 504, which overlies

10   a silicon oxide layer 502. Residue material 510 produced during preheating of the substrate,

11   and during patterned etching of the stack of the layers 500, resides in very large amounts on

12   the sidewalls 512 of hard mask 508 and on the sidewalls 514 of etched platinum-containing

13   layer 506. The substrate was preheated using a plasma generated from 120 sccm of Cl_2, 30

14   sccm of Ar, and 15 sccm of N_2, and is referenced in Table One as Run # 5. The platinum-

15   containing layer 506 was etched using the $Cl_2/N_2/Ar$ plasma source described in Table Two.

16   The process conditions were as described previously, above.

17   Figure 5B is representative of the comparative example in which the etch stack

18   described with reference to Figure 5A is preheated using an electrostatic chuck having a

19   resistive heater embedded therein. There was no plasma preheating of the substrate. The

20   platinum-containing layer 506 was etched using the $Cl_2/N_2/Ar$ plasma source described in

21   Table Two. The process conditions were as described previously, above. No residue was

22   present after etching of the platinum-containing layer 506. This clearly illustrates that the

23   residue material 510 observed with reference to Figure 5A was produced as a result of the

24   sputtering/etching of substrate etch stack material which occurred during the plasma

25   preheating of the substrate using a plasma generated from the $Cl_2/N_2/Ar$ plasma source gas.

26   Similar studies were made on a more limited basis for other etch stacks containing

1 metals or metal-containing compounds which are of low volatility, similar to platinum. In

2 particular, substrates containing etch stacks including either iridium or ruthenium dioxide

3 were preheated and etched in a manner similar to that described above. Either nitrogen or

4 oxygen was used to generate the plasma used to preheat the substrate. The etchant plasma

5 used to etch iridium was generated from a plasma source gas containing $O_2/Cl_2/CF_4$. The

6 etchant plasma used to etch ruthenium dioxide was generated from a plasma source gas

7 containing $O_2/Cl_2/Ar$. Although applicants were able to obtain etched iridium profiles which

8 appeared to be relatively free from sputtered metal-containing material, the overall etch

9 results in terms of etch rate, selectivity, and etch profile were less than desired. Work to

10 develop a satisfactory etchant plasma for etching iridium will have to be done prior to

11 determining the best plasma source gas for preheating of the substrates.

12 The etching of a ruthenium dioxide-comprising etch stack provided more

13 encouraging results, which are presented below.

14 Table Three. Ruthenium Dioxide-Containing Substrate Layer - Etch Profile

Run #	1	2
N_2 Preheat Gas (sccm)	100	--
O_2 Preheat Gas (sccm)	--	100
Etch Profile	Virtually Vertical	Virtually Vertical

19 Each substrate was preheated for about 45 seconds. Other preheating parameters

20 included a chamber pressure of about 20 mTorr; a substrate bias power of about 500 W; a

21 plasma source power of about 1800 W; and a cathode temperature of about 80°C.

22 Each ruthenium dioxide layer was plasma etched for about 60 seconds and thereafter

23 exposed to a diluted HF solution. The etchant plasma was generated from a plasma source

24 gas comprising 320 sccm of O_2, 80 sccm of Cl_2, and 20 sccm of Ar. Other process

25 parameters included an etch chamber pressure of about 36 mTorr; a substrate bias power of

20

1   about 200 W; a plasma source power of about 1500 W; and a cathode temperature of about

2   80°C.

3   In Runs # 1 and # 2, both plasma gases that were used to preheat the substrate (O_2

4   and N_2) produced similarly good results after the plasma etch and HF solution exposure.

5   Virtually all of the sputtered material was removed during the plasma etch step, thereby

6   producing a residue-free, essentially vertical etch profile.

7   The above described preferred embodiments are not intended to limit the scope of

8   the present invention, as one skilled in the art can, in view of the present disclosure expand

9   such embodiments to correspond with the subject matter of the invention claimed below.